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For More Information

Bo Brummerstedt Iversen, Department of Chemistry, University of Aarhus, Denmark

Email: bo@chem.au.dk

Physical Properties and 20 K Synchrotron X-ray Charge Density of a Magnetic Metal Organic Framework Structure, $\text{Mn}_3(\text{C}_8\text{O}_4\text{H}_4)_3(\text{C}_5\text{H}_{11}\text{ON})_2$

R.D. Poulsen, A. Bentien, M. Chevalier, and B.B. Iversen

Department of Chemistry, University of Aarhus, Denmark

Interest in metal organic frameworks (MOFs) has exploded recently due to the potential gas-storage applications of these nanoporous materials. Here we present an investigation of a new magnetic MOF, $\text{Mn}_3(\text{C}_8\text{O}_4\text{H}_4)_3(\text{C}_5\text{H}_{11}\text{ON})_2$, performed using a combination of physical properties measurements and x-ray charge density modeling. We found that the structure has an anti-ferromagnetic ordering at ~4 K. The electron density, determined from multipole modelling of 20 K single-crystal synchrotron x-ray diffraction data, provides a microscopic understanding of the macroscopic magnetic properties. Furthermore, it allows for a detailed analysis of the chemical bonding as well as the calculation of derived properties, such as the electrostatic potential.

Experimental determination of electron densities (EDs) demands x-ray diffraction data of high quality. In order to reduce systematic errors in the data, such as extinction and absorption, x-ray diffraction experiments are preferably carried out on very small crystal samples. Extinction and absorption effects are also reduced if high-energy radiation is used. Thus, synchrotron radiation is highly advantageous in accurate x-ray charge density studies. Proper description of thermal motion requires high-resolution data, and this necessitates the use of helium cryostats. Very low temperature experiments have the added benefit of drastically reducing thermal diffuse scattering (TDS) effects. If accurate data have been measured, the ED can be modeled using the multipole method. A Bader topological analysis of the ED provides a characterisation of the chemical bonding.

The structure of $\text{Mn}_3(\text{C}_8\text{O}_4\text{H}_4)_3(\text{C}_5\text{H}_{11}\text{ON})_2$, **1**, consists of 1D chains of carboxylate-bridged manganese atoms, which are interconnected by the organic benzene-1,4-dicarboxylate linker ($\text{C}_8\text{H}_4\text{O}_4$, BDC), forming rhombic cavities. A multitemperature structural characterization reveals a possible phase transition between 100 K and 20 K due to ordering of the diethylformamide molecules, ($\text{C}_5\text{H}_{11}\text{ON}$, DEF), bonded directly to the 1D chain and located in the rhombic cavities (**Figure 1**). The synthesis, physical property characterisation, and synchrotron x-ray charge density of a similar 1D manganese chain metal organic framework structure, $\text{Mn}_2(\text{C}_8\text{O}_4\text{H}_4)_2(\text{C}_3\text{H}_7\text{ON})_2$, **2**, have been reported previously¹. As for the structure of **1**, this framework also consists of rhombic cavities spanned by the BDC linker, which interconnect the 1D manganese chains. However, contrary to **1**, the magnetic susceptibility and heat-capacity measurements revealed no magnetic ordering down to 2 K.

The topological analysis of the EDs of **1** and **2** reveal that no direct Mn-Mn bonds are present. The magnetic ordering in **1** is due to super-exchange via oxygen bridges between the Mn atoms within the 1D chain, whereas the lack of ordering in **2** is the result of one bridge being an entire carboxylate group (**Figure 1**). The 3D ordering in **1** is due to the alignment of the BDC π -systems at low temperature. The analysis of the magnetic susceptibility and heat-



Authors (from left) Rasmus D. Poulsen, Bo B. Iversen, Anders Bentien, and Marie Chevalier

capacity data suggest Mn^{2+} ions for both **1** and **2**. However, the ED analyses reveal very different Mn centers in **1** and **2**. Orbital populations and a topological analysis show that both Mn atoms of **1** are almost neutral with a substantial anisotropy of the d-orbitals, whereas the Mn atoms of **2** are spherical, high-spin Mn^{2+} ions. The oxygen ligands have similar atomic properties in **1** and **2**, and the difference between the Mn charges is due to a reversed polarity of the carbon atoms (slightly positive in **1**, slightly negative in **2**).

It is somewhat surprising that two structurally similar MOFs have quite different chemical-bonding and atomic properties. The differences can be directly observed in the electrostatic potentials (**Figure 2**) calculated from the experimental EDs. For **1** the potential is fairly uniform, whereas the potential for **2** shows both negative and positive regions. Whether these observations can be correlated with the gas-absorption properties is not yet known, but future ED studies of similar MOFs will be of considerable interest.

¹R.D. Poulsen, A. Bentien, T. Graber, and B.B. Iversen, *Acta Crystallogr. Sect. A*, **60**, 382-389 (2004).

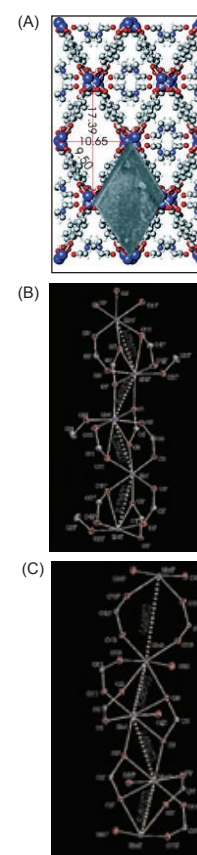


Figure 1. (A) A view of the crystal structure along the a-axis. In one of the nanopores an electron microscope image of a single crystal specimen is overlaid. Approximate pore dimensions are given in Å. (B) The 1D manganese chain of **1**. (C) The Mn-chain in **2**. The Mn-chain runs approximately along the a-axis. Thermal ellipsoids are drawn at 50% level, and in all figures the axes directions are shown with arrows.

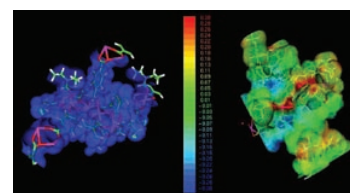


Figure 2. The electrostatic potentials of **1** and **2**, calculated from the experimental electron density and plotted on density isosurfaces of $0.01 \text{ e}/\text{\AA}^3$. The potentials are drawn with the same color coding, which ranges from $-0.3 \text{ e}/\text{\AA}$ (blue) to $0.3 \text{ e}/\text{\AA}$ (red).